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**Solid Oxide Fuel Cell Development at
Topsoe Fuel Cell A/S and Risø National Laboratory**

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The consortium of Topsoe Fuel Cell A/S and Risø National Laboratory has up-scaled its production capacity of anode-supported cells to about 1100 per week. Stacks are based on a compact thin plate multilayer design with metallic interconnects and 12x12 cm² or 18x18 cm² foot print. Larger (500 cm²) cells are currently under evaluation. Stacks have been tested successfully for more than 13000 h. Several 50 or 75 cell stacks in the 1+ kW power range have been tested successfully at a fuel utilisation of up to 92%. Multi stack modules consisting of four 75 cell stacks have been tested for more than 4000 h with pre-reformed natural gas and modules consisting of twelve stacks are under development. The degradation rate has been reduced to below 0.5% per 1000 h, especially by improvement of metal alloy interconnects and coatings. Our SOFC program comprises development of next generation cells with metallic support for operation at lower temperature. In this case porous ferritic steel is used as a cheap, ductile, robust cell support and the electrolyte is based on scandia-stabilized zirconia with improved durability. Furthermore, the metal supported cells offer a significantly improved tolerance towards redox cycling. In collaboration with Wärtsilä, a 24-stack prototype based on natural gas is being tested. For methanol based systems the methanol is methanated upstream the anode using a newly developed proprietary Haldor Topsoe catalyst. The range of fuels have further been extended to include ethanol and coal syn-gas by development of a new coke resistant catalyst suitable for future SOFC technology.

Background

Topsoe Fuel Cell A/S (TOFC) and Risø National Laboratory (Risø) are jointly carrying out a development programme focusing on low cost manufacturing of planar anode-supported cells and stacks employing metallic interconnects. The consortium of TOFC and Risø has up-scaled its production capacity of anode-supported cells to about 1100 cells per week. The consortium has an extended program to develop the SOFC technology all the way to a marketable product. The road to a successful SOFC technology is first and foremost governed by the ability to produce reliable and cost-effective cells and stacks.

Cell Development and Production

The production facility at Risø jointly operated by Risø and TOFC has now celebrated its 5 years anniversary. The number of anode supported cells (referred to as second generation cells, 2G) produced for development and demonstration of stack technology at TOFC and partners has increased rapidly as shown in . The number of cells produced in 2006 exceeded 12.000. The composition of the 2G cell has been frozen since 2004 and focus has been on improvement of the manufacturing process aiming at improved performance as well as reduction of rejection rate. The cell size has been scaled up such that cells in the size of $18 \times 18 \text{ cm}^2$ are routinely produced. The largest cell manufactured so far is 1250 cm^2 (1).

The 2G cell is based on the classical materials: LSM-YSZ cathode, YSZ electrolyte and Ni-YSZ anode and anode support. This cell type is very well characterized with respect to performance and durability (2). The average ASR at 850°C is $0.18 \pm 0.03 \Omega\text{cm}^2$ with a degradation rate below 0.6 \%/1000 h for current loads up to 1 A/cm^2 . However, to achieve the same high performance at lower temperatures, and to obtain an improved mechanical stability, new cell generations are also being developed. Two lines are currently being pursued: 1) improvement of cells based on Ni-YSZ anode supports and 2) development of metal supported cells, 3G.

Based on the 2G half cells, a cell for operation around 700°C is being developed with an LSCF cathode and a ceria barrier layer between the cathode and the YSZ electrolyte. New types of supports based on Ni-YSZ are also under development aiming at higher mechanical strength and improved redox stability (1,3). Examples of the achieved mechanical strength, as measured in a ball-on-ring biaxial test (sample diameter $\sim 2 \text{ cm}$) are given in Figure 2. The average biaxial strength of the 2G standard cells is 315 MPa with a “minimum strength” of 275 MPa , and as is evident from Figure 2, the mechanical strength can be improved considerably up to a “minimum strength” of 350 MPa by modification of the manufacturing parameters (4).

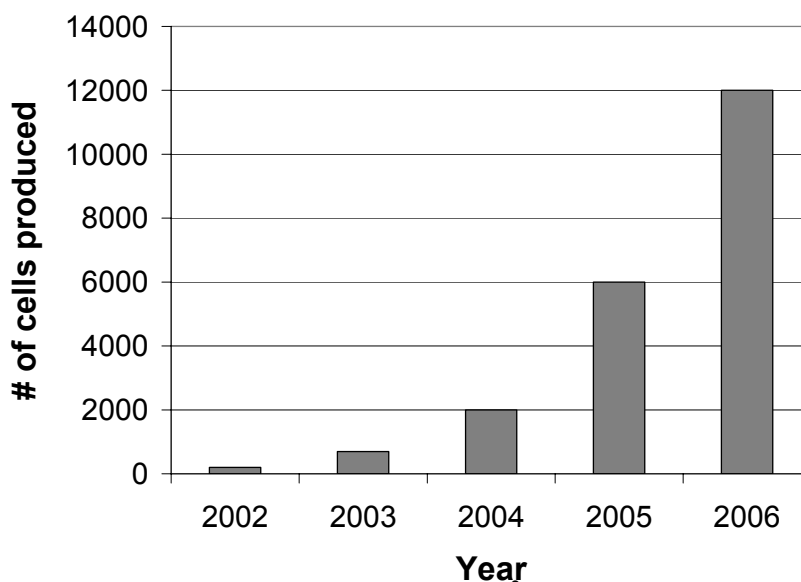


Figure 1. Number of anode supported $12 \times 12 \text{ cm}^2$ cells produced per year from 2002 to 2006.

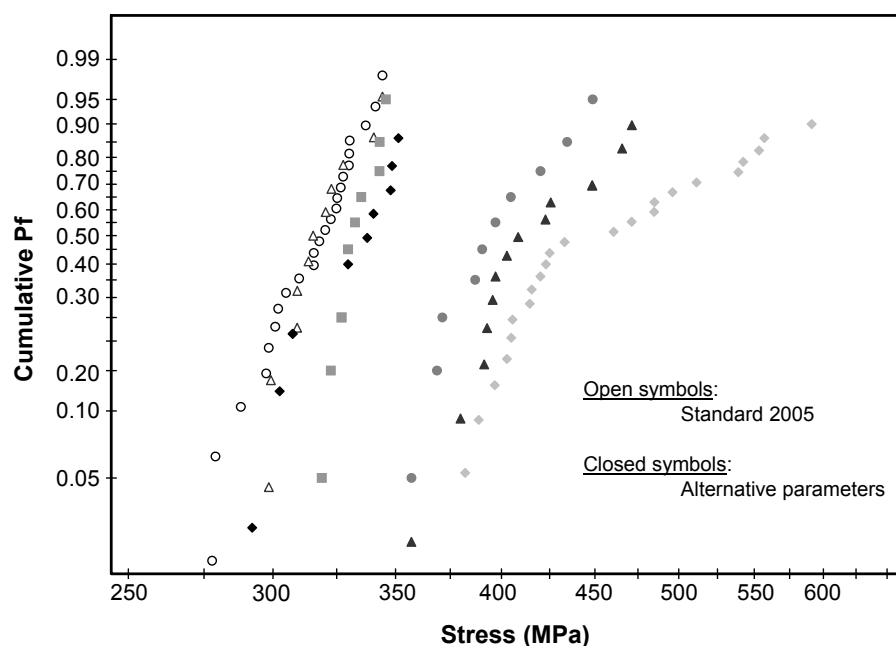


Figure 2. Statistical distribution (Weibull plot) of mechanical strength data for various anode supports

The pre-pilot production relies on a spraying process for cathode deposition (5). Due to the ease of up-scalability and with the aim to further improve the reproducibility of the cell production (2), screen printing is being investigated as an alternative route. Cathode performances measured on screen printed cathodes (symmetrical cells based on 150 μm zirconia tapes) are compared to sprayed ones in Figure 3 (6). Evidently, the screen printed cathodes match the sprayed cathodes, and this process is thus considered for use on future large area cells.

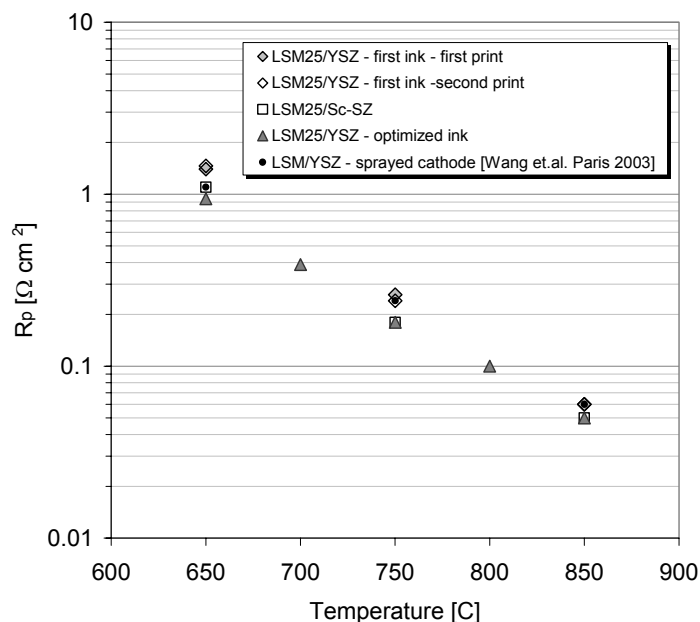


Figure 3. R_p values for symmetric cells with YSZ/LSM cathodes on YSZ electrolyte. A cathode with ScSZ is also shown for comparison. Sprayed cathode from Wang et al (7) .

A completely new cell type based on a FeCr alloy support for operation below 700 °C is also being developed. For this cell type it is not only the support material that is new; cathode, electrolyte and anode are also based on a new materials choice. So far 3G cells up to 12x12 cm² have been manufactured successfully. However, the electrical performance still lacks behind that of the anode supported cell.

2G Cell durability

The 2G cells manufactured in the production line are generally very durable at high temperature (850 °C) even at very high current loads (8). The degradation rate increases with increasing polarization. At a current density of 0.25 A/cm² (operating voltage ~ 850 mV) the voltage degradation rate is less than 0.25 %/1000 h and at 1 A/cm² (corresponding to an operating voltage ~ 750 mV) the degradation is below 0.6 %/1000 h (See also Figure 5, upper curve). Operating the cells at 750 °C also provide excellent durability when operating at normal polarization levels. However, under severe operating conditions at 750 °C, i.e. exposed to a strong polarization, a marked degradation is observed. This degradation has been identified to mainly originate from the cathode/electrolyte interface (8, 9). Efforts are being devoted to develop cells that are also capable of long term operation under these conditions, to enhance the window of operation of the technology. Recently, progress has been achieved in this field. Figure 4 shows the cell voltage of the standard 2G cells as well as a cell with a modified cathode as a function of operating time under high polarization at 750 °C. The introduced modification of the cathode effectively results in stable operation, even under these severe conditions, after an initial degradation occurring over the first 500 h.

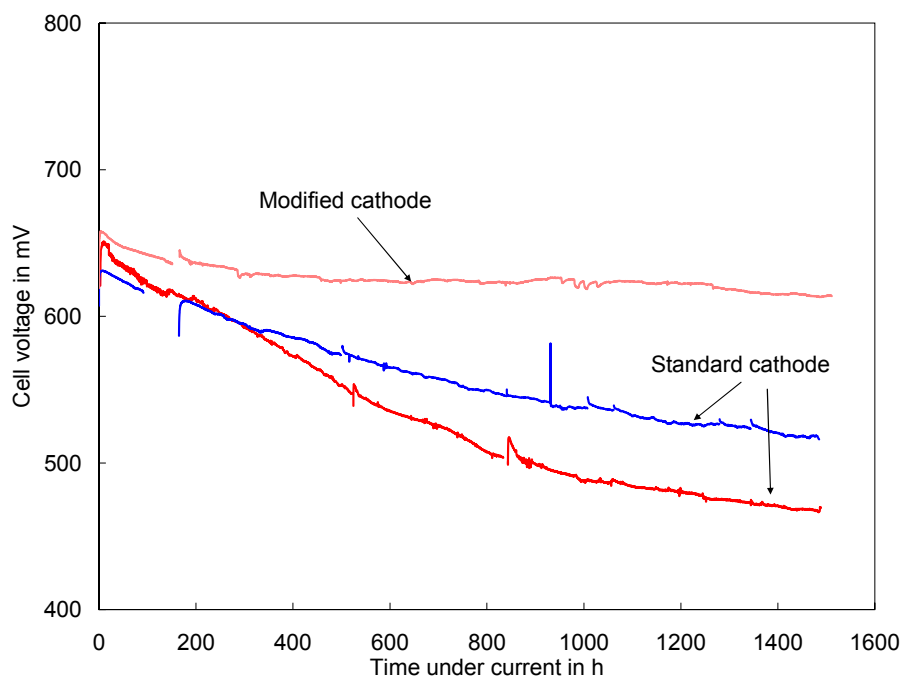


Figure 4. Stability of modified LSM cathodes in accelerated aging test (“low temperature, high polarization”). The temperature was 750 °C, the current density was 0.75 A/cm², and the cells operated on a syn-gas mixture with a fuel utilization of ~80 %.

Effect of Sulphur on Cell Durability

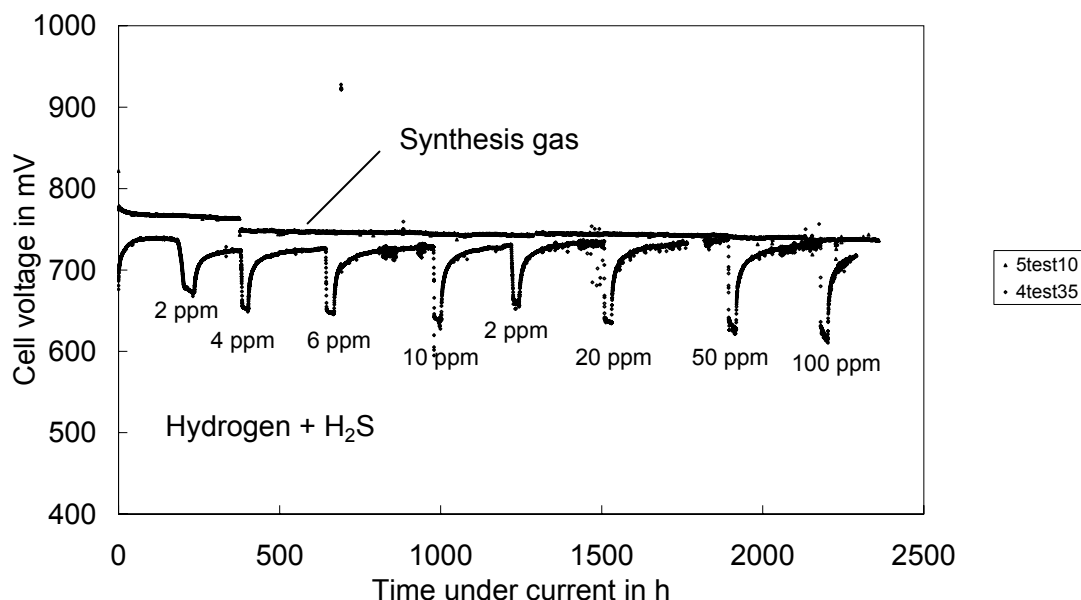


Figure 5. Cell durability at 850 °C, 1A/cm². The upper curve is for a cell operated in syn-gas with a fuel utilization of 75 %. The lower curve is for a cell operating at the same temperature and current load but in hydrogen with various amounts of H₂S added periodically.

When using fuel derived from biomass in SOFCs, one must be aware of trace amounts of different impurities which may act as poison for the electrochemical processes. One such impurity is H₂S, which is also used as odorant in natural gas lines. The sulphur tolerance of the anodes is currently studied. The effect of small amounts of H₂S in hydrogen on the performance and durability of a “standard” 2G cell was studied at 850 °C and 1 A/cm² (see Figure 5). The cell voltage decreased and the degradation rate increased during the periods under H₂S. However, these changes were completely reversible up to the studied concentration of 100 ppm H₂S (10). Turning off the sulphur addition results in a recovery of the cell performance over a period of ~250 h, and the overall degradation tracked over 2000 h is less than for the reference case. Thus, it is concluded that the sulphur reduces the reaction rate by passivation of reaction sites by adsorption.

Stack Development and Production

Due to the very compact stack design including thin-plate metallic interconnects, a stack volume power density of 2.4 kW per litre stack volume has been obtained in cross-flow configuration with hydrogen fuel at 0.35 W/cm². Standard stacks have been tested successfully for more than 13000 h. Post-mortem analyses have revealed the dominating degradation mechanisms. Recently, the degradation rate has been reduced to below 0.5% per 1000 h by introduction of improved stack component materials, including improved metallic interconnects. Several 50- or 75-cell stacks in the 1+ kW power range have been tested successfully on methane rich reformat gas at a fuel utilisation up to 92%. Figure 6 shows the I/V performance of a 75-cell (12x12 cm²) stack with counter flow

configuration. Stack and system modelling including cost optimisation analysis is used to develop 5-25 kW stack modules for operation in the temperature range 700-850°C.

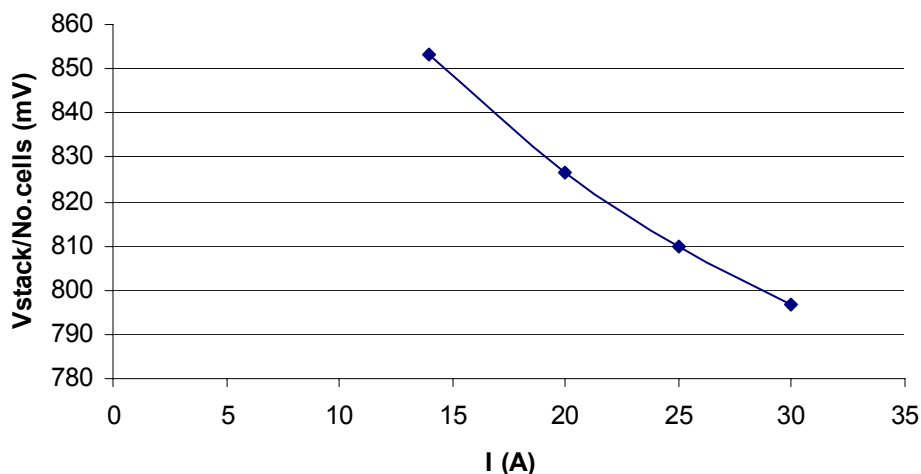


Figure 6. I/V performance of a 75-cell (12x12 cm²) counter flow at 800°C, 65% fuel utilisation with pre-reformed natural gas.

A special effort is focused on manufacturing and testing of larger anode-supported cells and stacks with a foot print of 18x18 cm². Figure 7 shows the performance of a seven-cell stack with 18x18 cm² cells operated at 800°C. It is seen that at a steady state current of 45 A, the degradation rate is below the detection limit after 500 h for both H₂ and CH₄ fuels.

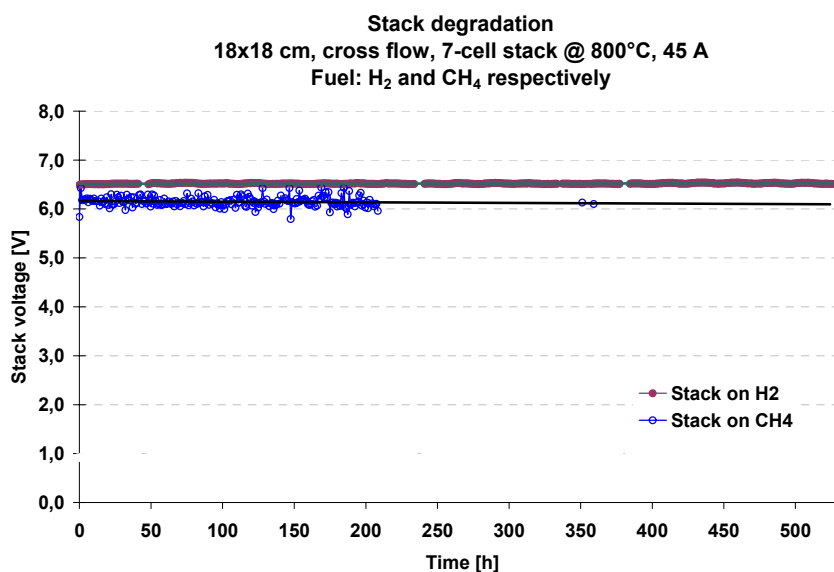


Figure 7. Degradation curves for 18x18 cm² cell stack, H₂/N₂ fuel (upper curve) and CH₄/H₂O (lower curve), steady state current 45 A.

Next Generation Stacks and Hot Box Modules

The next generation stacks include an improved integrated metallic interconnect design aiming at further weight saving, cost reduction and reduction of internal stack pressure drop. An integrated hot box 1,8 kW_{el} module, including new stack design, stack clamping system and thermal insulation has been developed and is currently tested by UTRC under a US Air Force demonstration project.

Further stack generation development is based on cells with metallic support as described above. The stacks are tailored to minimize parameters such as weight, pressure drop, start-up time and cost and to maximize robustness, durability, performance and redox stability.

Fuel Processing and System Development

A range of fuels have previously been studied including natural gas, LPG, methanol, DME, diesel and ammonia. The studies predict system electrical efficiencies from 50-56% (AC out/LHV fuel in), depending on the fuel used and the size of the system. The range of fuels have now been extended to include ethanol and coal syn-gas (11) by development of a new coke resistant ethanol reforming/methanation catalyst and leveraging the catalyst know-how of HTAS involved in high temperature methanation of coal gas respectively.

TOFC has collaborated with Wärtsilä since 2002 on the development of SOFC systems in the 200+ kW class, primarily for power generation and marine application. Since late 2004 Wärtsilä has operated the SOFC test system with planar SOFC stacks developed and manufactured by TOFC. During spring 2006 four stacks were installed, each having a nominal power of 1 kW. The system has been in continuous operation providing an average power of 3.6 kW at 55 – 60 % fuel utilisation (FU), this being a valid reference point for further system development and up-scaling. The in total 4000 h of operation indicates very good reliability of the used stack and system technologies. In Figure 8, the power curve combined with average FU for the four stacks is presented (12).

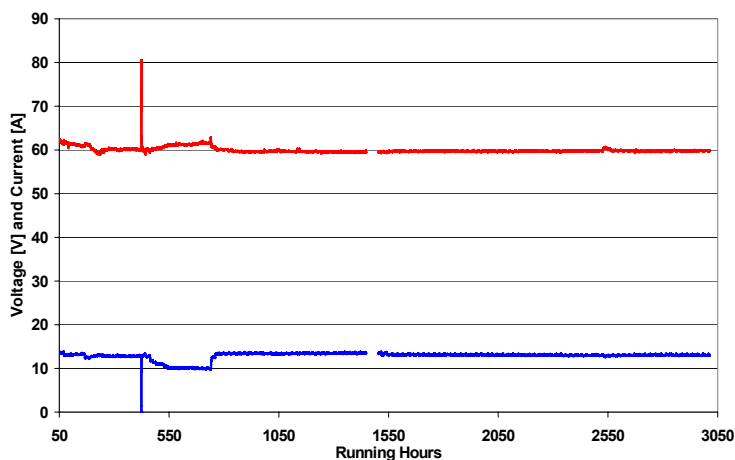


Figure 8. Average stack voltage (upper curve) and current (lower curve) of 75-cell stacks in a four stack system.

In collaboration with Wärtsilä, a detailed design for a 24-stack prototype based on natural gas has been finalised and 24 stacks of the 75 cell (12x12 cm²) type to Wärtsilä by TOFC. Another 24-stack prototype, now based on methanol as the fuel, is also under construction by Wärtsilä. The methanol is methanated upstream the anode, using a newly developed, proprietary Haldor Topsoe catalyst.

Two Danish projects in the PSO program supported by the Danish Utilities have been initiated. One is aiming at demonstrating a 1 kW_e micro-CHP unit and the other is a 10 kW_e stack demonstration facility including fuel processing and power conversion located at a power station in Copenhagen, Denmark.

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